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EXPERVIRIAL THEOREMS AND THE HELLMANN-FEYNMAN

THEOREM IN DIFFERENT COORDINATE SYSTEMS

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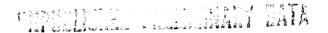
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HYPERVIRIAL THEOREMS AND THE HELLMANN-FEYNMAN THEOREM IN DIFFERENT COORDINATE SYSTEMS*

bу

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Abstract

It is shown that the difference between the Hellmann-Feynman theorems in two different coordinate systems is in general a hypervirial theorem.



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Recently $^{1-4}$ there has been considerable interest in the fact that the Hellmann-Feynman theorem takes different forms depending on the coordinate system one uses. Thus if we are using coordinates $\mathbf{X}_{\mathbf{K}}$ and if λ is a parameter then the (generalized) Hellmann-Feynman theorem may be written

$$E' = (\psi_x, H'_x \psi_x)$$

where we have denoted differentiation with respect to λ by a prime and where the subscript x on ψ and H is to remind us that they are the wave function and Hamiltonian appropriate to the X_k coordinate system. Similarly if we use coordinates Y_k we have

from which we infer that

$$(4x, H'_{x}, 4x) - (4x, H'_{x}, 4x) = 0$$
 (1)

For the example discussed in references 1-3 eq. (1) has been found to be the virial theorem. In the example discussed in reference 4 eq. (1) is found to be again of a similar form. It is the purpose of this note to show that in general eq. (1) is a hypervirial theorem. To do this we assume 6 that the transformation from the \times k

system to the $\frac{\gamma_{k}}{k}$ system can be accomplished by means of a unitary transformation $^{7-8}$

$$\Psi_{Y} = \Psi_{X} \tag{2}$$

$$H_{\gamma} = U H_{\kappa} U^{\dagger}$$
 (3)

From this it follows that

$$H_{y}' = 0' H_{x} U^{\dagger} + U H_{x}^{\prime} U^{\dagger} + U H_{x} U^{\dagger}^{\prime}$$
 (4)

We now make use of $U^{\dagger}U=1$ to find

Using this eq. (4) becomes

Thus using eq. (2), eq. (1) may be written

$$(\psi_{x}, (U^{\dagger}U^{\dagger}, H_{x}) \psi_{x}) = 0$$
 (5)

which <u>is</u> the hypervirial theorem for U^{\dagger} .

To write down a general formula for $U^{\dagger}U^{\prime}$ would be quite complicated. However for the examples discussed in references 1-4 it is sufficient (see footnote 6) to consider simple scalings $\chi_{\mathbf{k}} = \lambda \, \gamma_{\mathbf{k}}$. For this case it is known (see for example reference 8a) that

$$U^{\dagger}U^{\dagger} = \frac{i}{2 \ln \lambda} \sum_{k=1}^{s} (P_k X_k + X_k P_k)$$

where $P_{\mathbf{c}}$ is the momentum canonically conjugate to $X_{\mathbf{c}}$, and where we have scaled s coordinates. When inserted into eq. (5) this yields the results which we have already mentioned, though it is by no means the simplest way of deriving them.

Footnotes and References

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- 2. P. Phillipson, J. Chem. Phys., 39, 3010 (1963).
- 3. A. C. Hurley in Molecular Orbitals in Chemistry, Physics and
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- 4. M. L. Benston, Bull, A.P.S., 10, 102 (1965).
- 5. J. O. Hirschfelder, J. Chem. Phys., <u>33</u>, 1762 (1960).
- 6. Since this assumption implies that $\chi_{\mathbf{k}}$ and $\chi_{\mathbf{k}}$ have the same range of values it would appear that the subsequent analysis will have restricted applicability. Happily this is not the case. Namely our analysis also applies to any coordinates $\mathbf{Z}_{\mathbf{k}}$ which are λ independent functions of the $\chi_{\mathbf{k}}$ since this will mean that the Hellmann-Feynman theorem takes the same form in the $\mathbf{Z}_{\mathbf{k}}$ and $\chi_{\mathbf{k}}$ coordinate systems.
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- 8. P. Jordan, Zsf. Phys., 37, 383 (1926), 38, 513 (1926).
- See also (a) S. T. Epstein, and J. O. Hirschfelder, Phys. Rev.,
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